

Li-Ion Battery Anodes from Electrospun Nanoparticle/Conducting Polymer Nanofibers

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Project ID ES264

Overview

Timeline

- October 1, 2016
- September 30, 2018
- Percent complete: 50%

Budget

- Total project funding
 - DOE \$590,000
 - Contractor \$117,062 (VU)
- Funding received in FY 2016: \$330,000
- Funding for FY 2017: \$273,259

Barriers

- Barriers addressed
 - Capacity fade when using Si as the anode material in a Li-ion battery
 - Achieving high volumetric, gravimetric, and areal energy densities at moderate C-rates
- Targets
 - Gravimetric capacity: 1,200 mAh/g (0.1C)
 - Areal capacity: 3 mAh/cm² (0.1C)
 - Volumetric capacity: 800 mAh/cm³ (0.1C)
 - 40% capacity retention at 2C

Partners

- Lawrence Berkeley National Lab
- Oak Ridge National Lab
- e-Spin Technologies, Inc.
- Project Lead: Peter N. Pintauro, Vanderbilt

Project Relevance and Objectives

Project Objective:

To fabricate and characterize nanofiber anode mats containing Si nanoparticles and an electronically conductive binder for Li-ion batteries, where the mats exhibit:

- High gravimetric, areal, and volumetric capacities
- Long cycle life (90% capacity retention after 200 cycles at 0.1C)
- Good performance at high C-rates (e.g., 500 mAh/g at 2C)

Relevance:

Address problems with conventional thin film Si slurry anodes: (i) Low area capacity (the need to use only thin electrodes), (ii) Poor volumetric and/or areal energy densities at high C-rates, (iii) Si expansion/contraction result in electrode deterioration during cycling.

2016-2017 Project Tasks/Goals:

1. Single fiber anode composed of Si/C/PAA
1. Si/C/PAA anode and $\text{LiCoO}_2/\text{C}/\text{PVDF}$ cathode in a full cell
2. Slurry and fibers anodes with Si and PFM/PEFM conductive binder
3. Dual fiber anode (Si/PAA and C/PAA fibers)
4. Droplet-fiber anode (Si/PFM droplets and C/PAA nanofibers)

Milestones

Month/Year	Milestone or Go/No-Go Decision	Status
September 2016	<u>Go/No-Go Decision</u> : Demonstrate an initial capacity above 500 mAh/g and 90% capacity retention after 50 cycles at 0.1C rate.	Complete
December 2016	<u>Milestone</u> : Demonstrate that at least one new conductive binder has been synthesized and is ready in sufficient quantity for electrospinning	Complete
March 2017	<u>Milestone</u> : Demonstrate at least one successfully electrospun composite anode containing at least 65% Si and/or SiO particles	Complete
June 2017	<u>Milestone</u> : Identify key structure/performance correlations for electrospun anodes	On track
September 2017	<u>Go/No-Go Decision</u> : Demonstrate a discharge capacity above 750 mAh/g, after 50 cycles at 0.1C and a capacity above 500 mAh/g after 50 cycles at 1C.	On track

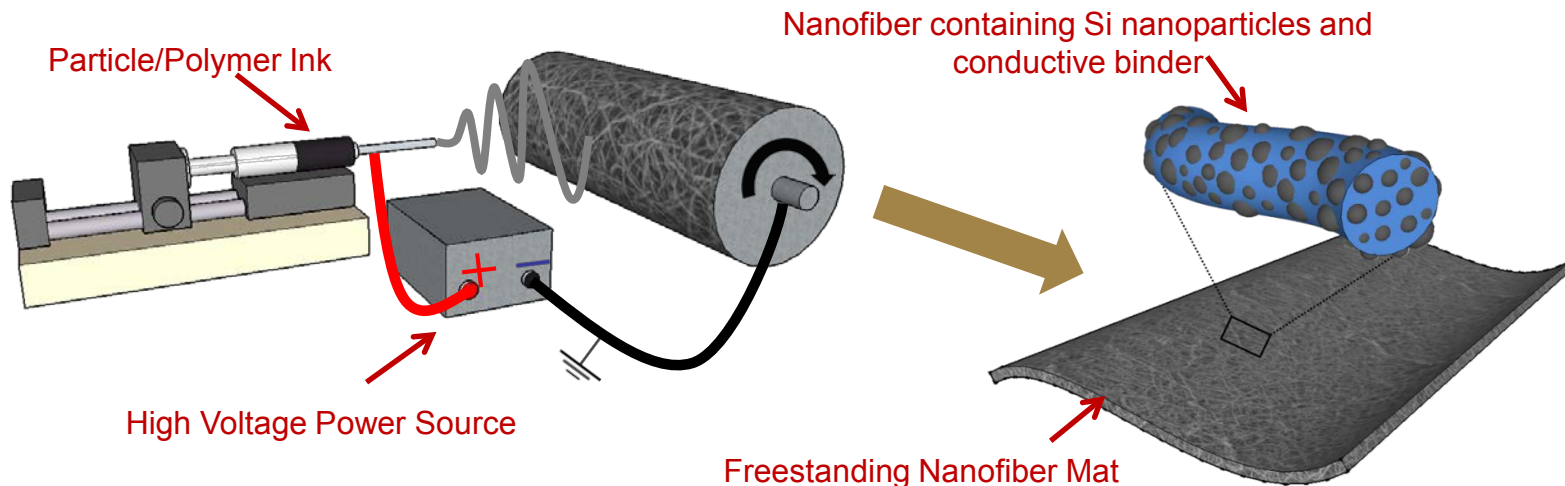
Particle/Polymer Electrospinning

Electrospun nanofiber anodes:

- Si nanoparticles with conductive polymer binder from G. Liu at LBNL
- Si nanoparticles with carbon powder and PAA
- Dual fiber mats (Si/PAA fibers and C/PAA fibers)

Advantages of a Nanofiber Mat Anode:

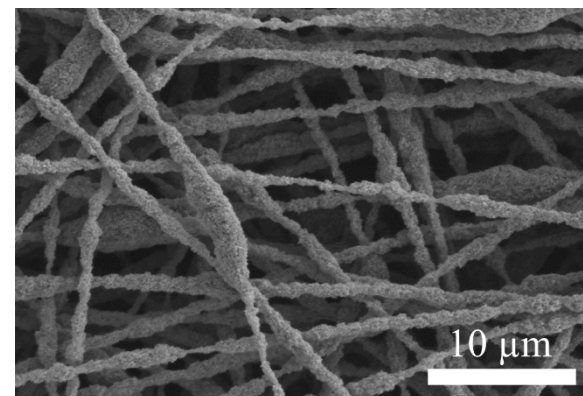
- High surface area/volume ratio
- Short Li^+ transport pathways
- Controllable fiber volume fraction (for high volumetric capacity)
- Utilize thick electrodes (for high areal capacity)
- Method is robust and can accommodate different Si sizes and binder formulations



Electrospun Si/C/PAA Single Fiber Anodes

Advantages of Si-based particle/polymer fiber mat structure

- Fibers with high Si loading can be electrospun
- Interfiber void space can accommodate Si volumetric changes during cycling
- Polymer binder with appropriate functional groups can interact with SiO_x layer on Si



Electrospinning conditions

- 1.00 mL/h
- 8 kV
- 8 cm spinneret-to-collector distance
- 20% relative humidity

Electrospun Fiber Composition

- 40 wt% Si nanoparticles
- 25 wt% carbon black
- 35 wt% poly(acrylic acid) (PAA)
- Fiber diameter $\sim 1 \mu\text{m}$

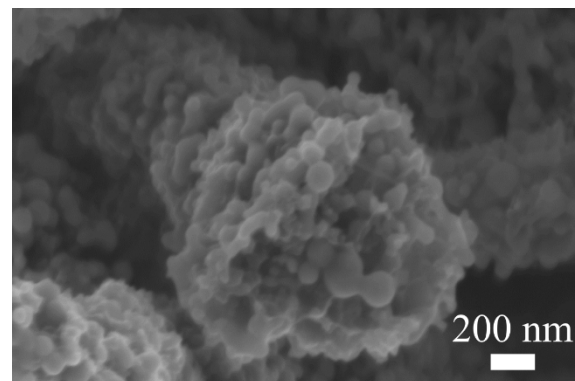


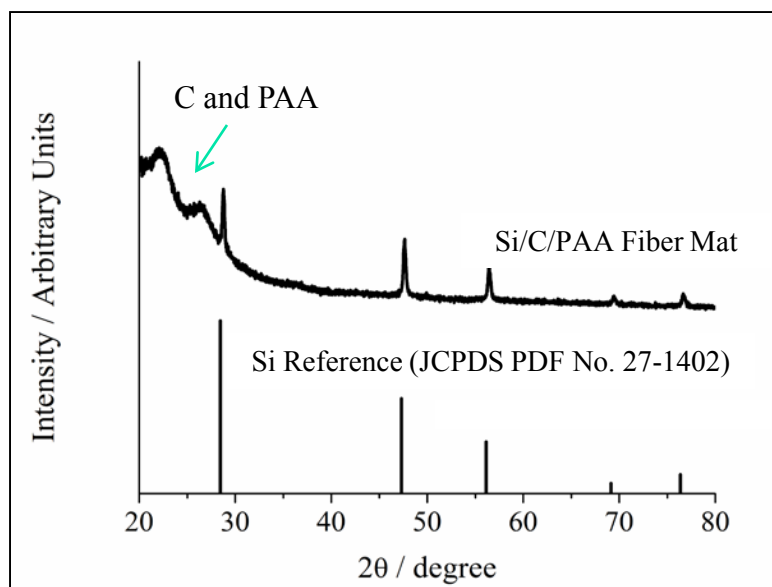
Image provided by Michael Naguib at ORNL.

Si/C/PAA nanofibers were successfully electrospun with a uniform particle distribution and an average fiber diameter $\sim 1 \mu\text{m}$.

XRD and EDX Characterization of Si/C/PAA Fiber Mats

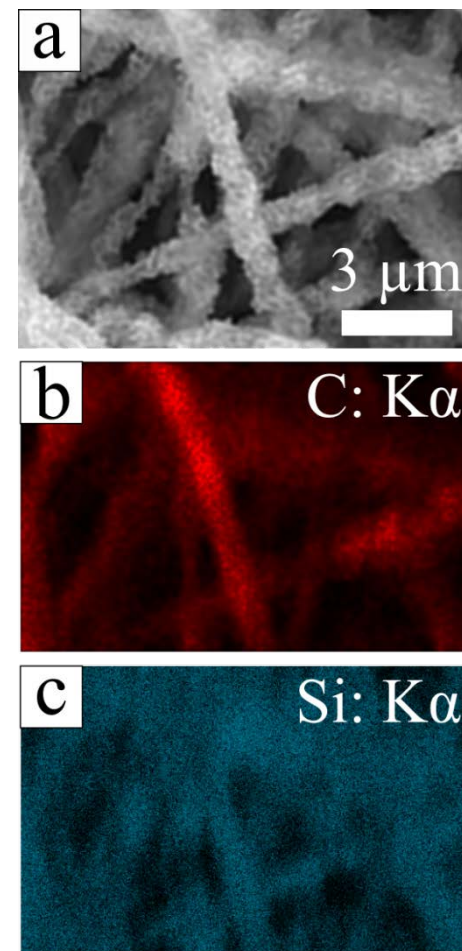
The structure of electrospun Si/C/PAA fiber mats was evaluated using x-ray diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDX).

XRD of Si/C/PAA Fiber Mat



XRD and EDX analyses demonstrate that Si and C are well-distributed throughout the electrospun fiber mats.

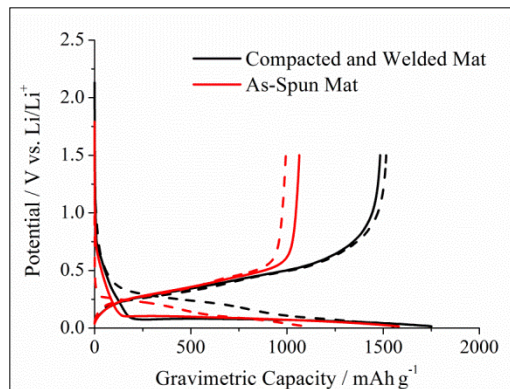
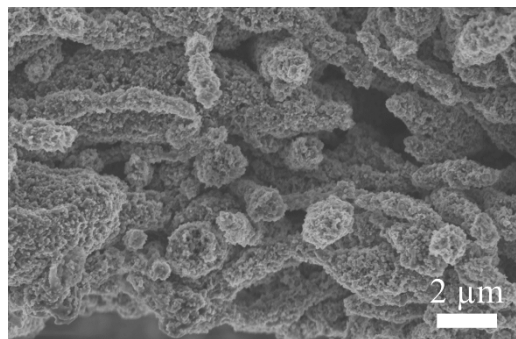
EDX Mapping of Si and C



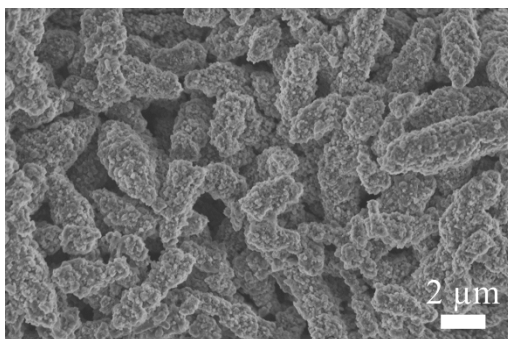
Performance of Si/C/PAA Nanofiber Mat Anodes in Half Cells

Si/C/PAA nanofiber anodes were tested in CR2032 half cells using a Li metal counter/reference electrode, Celgard 2500 separator, and an electrolyte containing 1.2 M LiPF₆ with 3/7 EC/DEC and 30% FEC additive

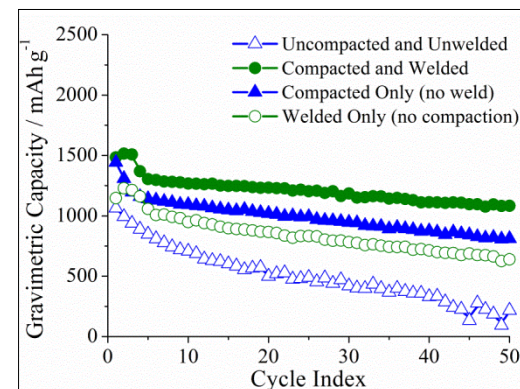
Fiber Mat Before Cycling



After 50 Cycles



SEM images provided by
Michael Naguib at ORNL



Areal Capacity: 4.5 mAh/cm²

Volumetric Capacity: 750 mAh/cm³

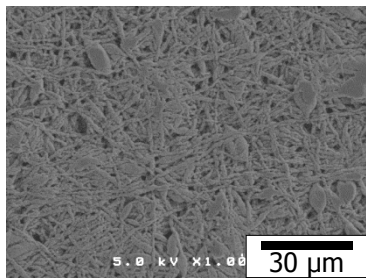
- Compacting and welding significantly improved anode capacity and cycling stability
- Both compaction and welding steps are needed to achieve best performance
- Fiber structure was preserved during cycling

Full Cell with Electrospun Anode and Cathode

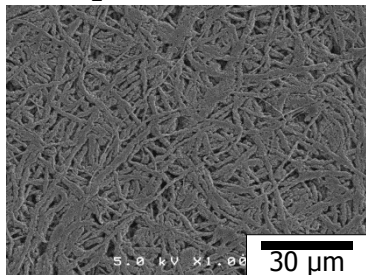
Full cells containing an electrospun particle/polymer anode and cathode were characterized

- Si/C/PAA (40/25/35) fiber mat anode
 - LiCoO₂/C/PVDF (70/10/20) fiber mat cathode
- Electrode loadings adjusted such that areal capacity was ~2.6 mAh/cm² at 0.1C

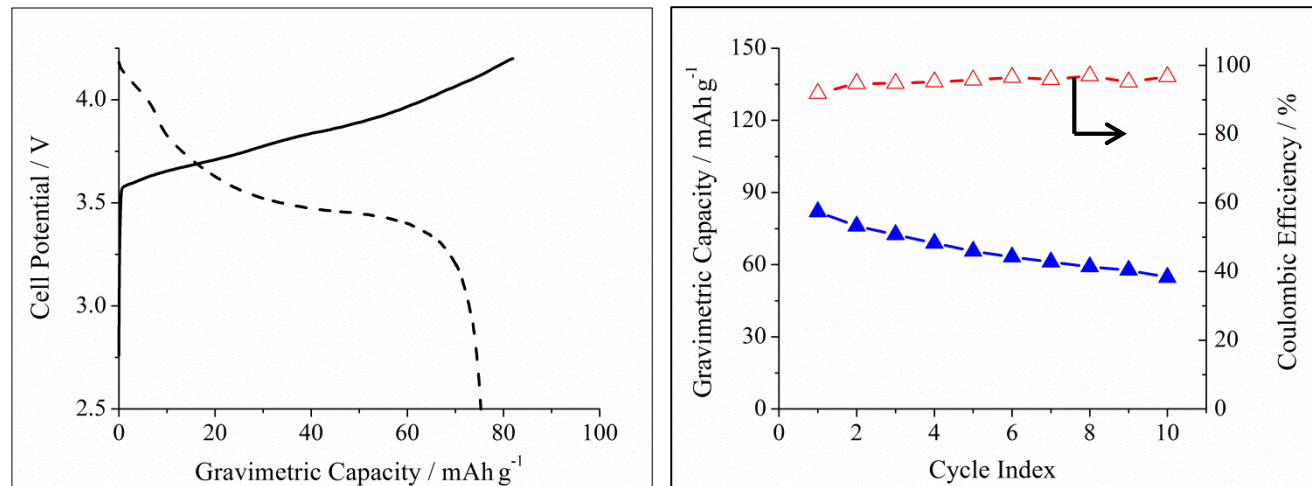
Si/C/PAA Anode



LiCoO₂/C/PVDF Cathode



Charge/Discharge cycling from 2.5 – 4.2V at 0.1C

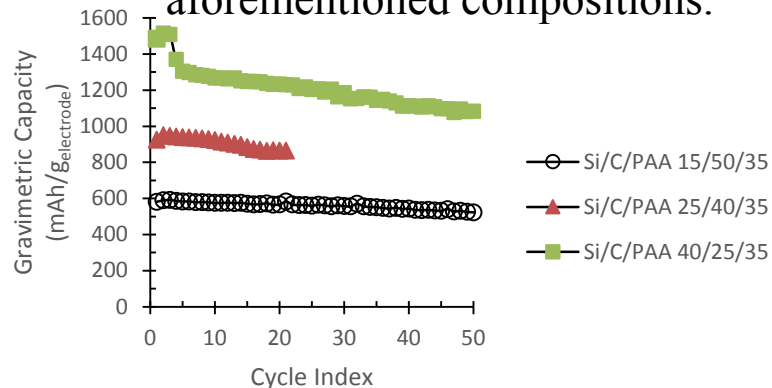


Results: An electrospun Si/LiCoO₂ full cell had a high specific energy density of 270 Wh/kg and areal capacity of 2.6 mAh/cm².

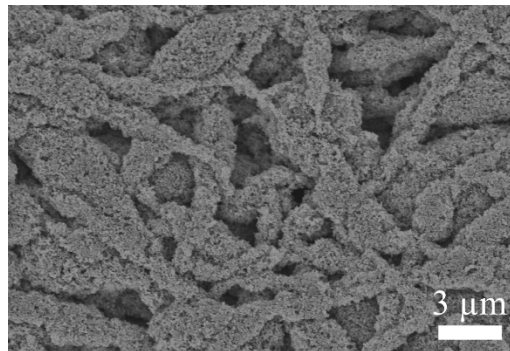
The Effect of Si Content in Electrospun Fibers on Cycling Stability

M4 Go/No-Go Milestone: 500 mAh/g and $\geq 90\%$ capacity retention after 50 cycles.

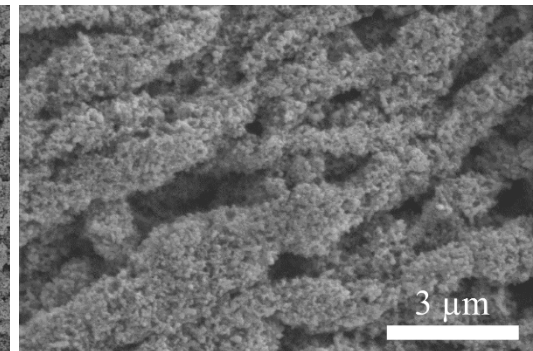
- This goal was achieved by decreasing the Si content in the fibers. Fibers containing 15 wt% Si (Si/C/PAA weight ratio of 15/50/35) were prepared and characterized.
- No change in the fiber mat morphology when the Si content was reduced; interfiber and intrafiber porosity was maintained.
- To better understand the relationship of electrode composition, fibers containing 25% Si (Si/C/PAA weight ratio of 25/40/35) were also fabricated with similar porosities as the aforementioned compositions.



Si/C/PAA: 15/50/35



Si/C/PAA: 40/25/35



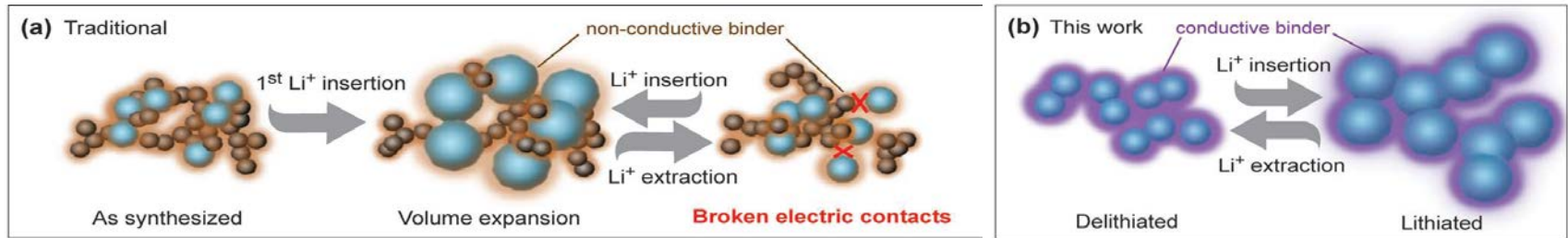
All 3 anodes had a capacity $\sim 3,200$ mAh/g_{Si} when normalized to the active material mass
→ Good active material utilization for both anodes

Anode with 15 wt% Si retained 90% of its initial capacity after 50 cycles at 0.1C

An electrospun anode containing 15 wt% Si had good cycling stability with an areal capacity of 1 ± 0.1 mAh/cm². Project milestone was achieved on schedule.

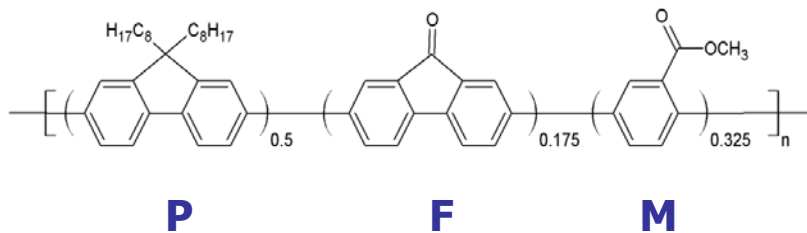
Electrically Conductive PFM and PEFM Binders

Use conductive binders that adhere to Si surface to prevent electrical isolation of Si particles during charge/discharge cycling.



PFM and PEFM polymers from Gao Liu, LBNL:

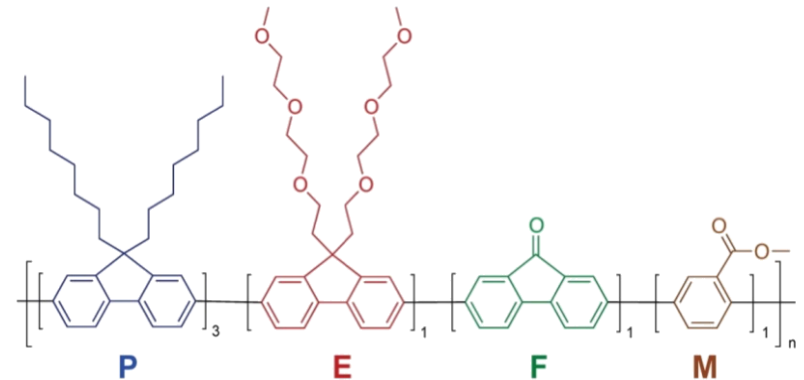
Poly(9,9-dioctylfluorene-co-fluorenone-co-methylbenzoic ester)



- Electrical Conductivity $\sim 1 \times 10^{-5}$ S/cm
- Swelling in Battery Electrolyte ~ 10 wt%

[1] G. Liu et al., *Adv. Mater.* **2011**, 23, (40), 4679-83.

[2] M. Wu et al. *J. Am. Chem. Soc.* **2013**, 135, (32), 12048-56.



PEFM is a modified version of PFM. It has sidechains for better polymer entanglement in solution (better electrospinning with Si) and better electrolyte sorption (for improved Li⁺ transport).

Electrochemical Performance of Si/PFM Anodes: Nanofibers and Slurry

Si/PFM anodes (slurry cast and electrospun) were tested in CR2032 half cells using a Li metal counter/reference electrode, Celgard 2500 separator, and an electrolyte containing 1.2 M LiPF_6 with 3/7 EC/DEC and 30% FEC additive

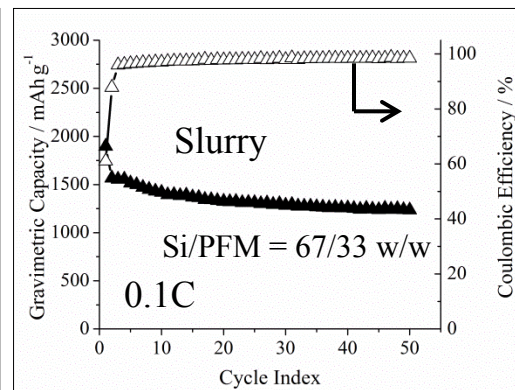
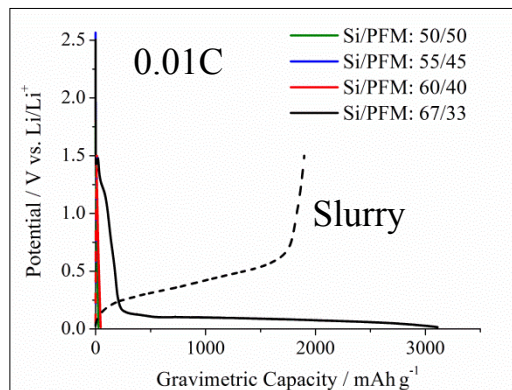
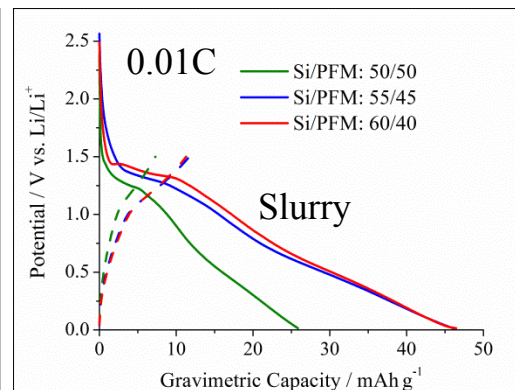
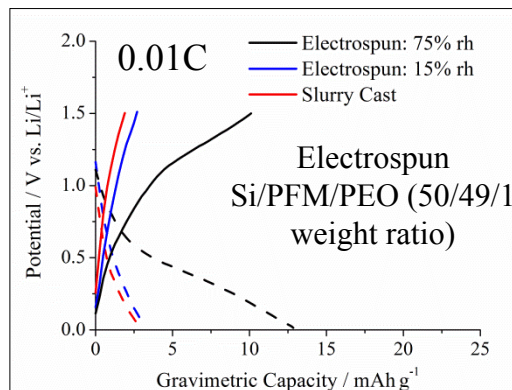
Si/PFM anodes with 50 wt% Si had capacities $< 15 \text{ mAh/g}$ even at 0.01C

- Similar results obtained for slurry cast and electrospun anodes
- Presence of PEO did not affect performance

Si/PFM slurry cast anodes containing 50-67 wt% Si were tested.

- Anodes with 50 – 60 wt% Si had very low capacities ($< 15 \text{ mAh/g}$)
- Anodes with 67 wt% Si (33 wt% PFM) displayed high reversible capacity and good cycling stability over 50 cycles.

Electrospun and Slurry Cast Si/PFM Anodes



Si/PFM anodes must contain $\leq 33 \text{ wt\%}$ PFM to ensure good electrochemical performance. Too much binder content may form a thick, ionically insulating coating on Si nanoparticles.

Performance of Si/PEFM Slurry Cast Anodes

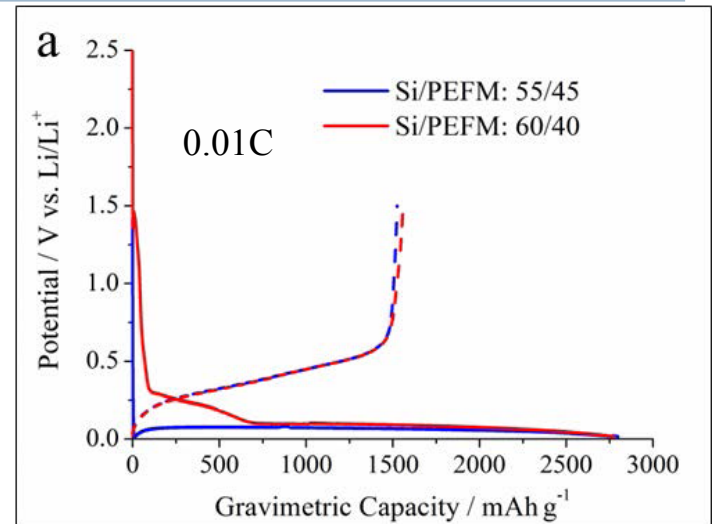
Slurry cast Si/PEFM anodes with 50 - 60 wt.% Si were tested in half cells.

- Anodes with 55 - 60 wt% Si had high reversible capacities $\sim 1,500$ mAh/g at 0.01C
- After 50 cycles at 0.1C, an anode with 60 wt% Si had 80% capacity retention.

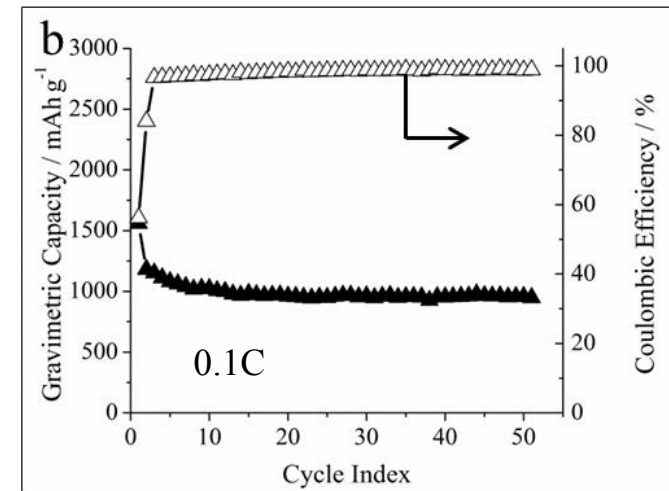
Target composition for electrospun Si/PEFM fibers is 55 wt% Si + 45 wt% PEFM (vs. 67 wt% Si + 33 wt% PFM)

With more PEFM binder, there is a high probability of electrospinning well-formed fibers.

Si/PEFM anodes showed good electrochemical performance. Compared to PFM, the presence of PEO side groups in PEFM allows for more swelling with electrolyte, thus improving Li^+ transport to active material.



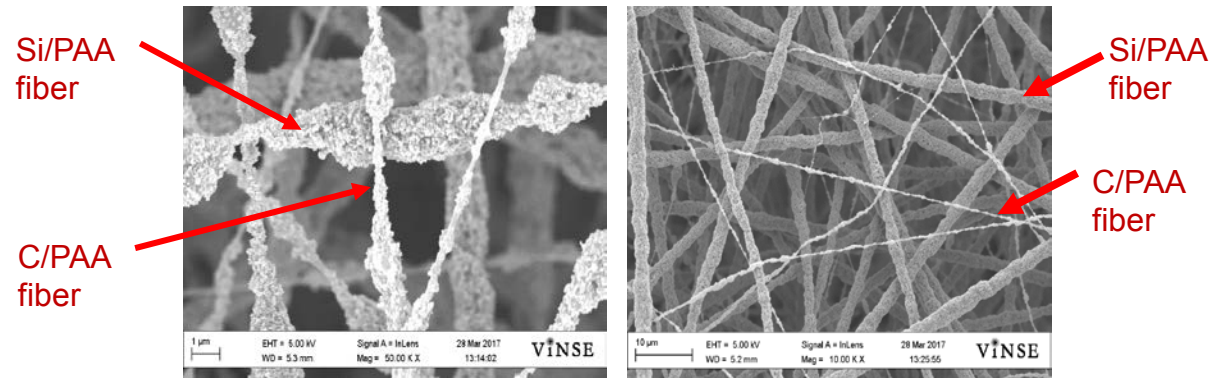
Si/PEFM = 60/40 w/w



Dual fiber electrospinning: Si/PAA Fibers and C/PAA Fibers

Simultaneously electrospin Si/PAA fibers and C/PAA fibers onto a common current collector. The Si/PAA and C/PAA weight ratios were the same, at 65/35. the weight ratio of Si to C fibers was 2:1, 1:1, and 1:2.

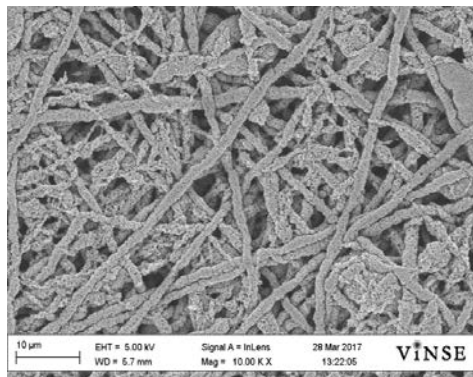
- The quality of Si fibers is good, with an average fiber diameter of 1-2 μm .
- The quality of C-fibers is fair/poor (a non-uniform distribution of carbon particles along the fiber length).



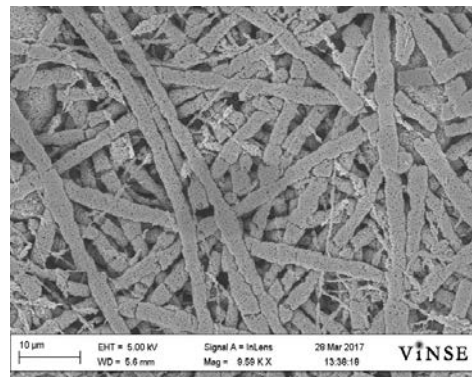
1:1 Si:C wt% ratio; fiber vol fraction 0.07-0.10

Compacting and Welding Fiber Mats: Electrospun mats were mechanical compacted at 90 MPa for 60 sec at room temperature, followed by welding by exposure to methanol vapor for 1 hour.

1:1 Si/PAA:C/PAA fiber ratio



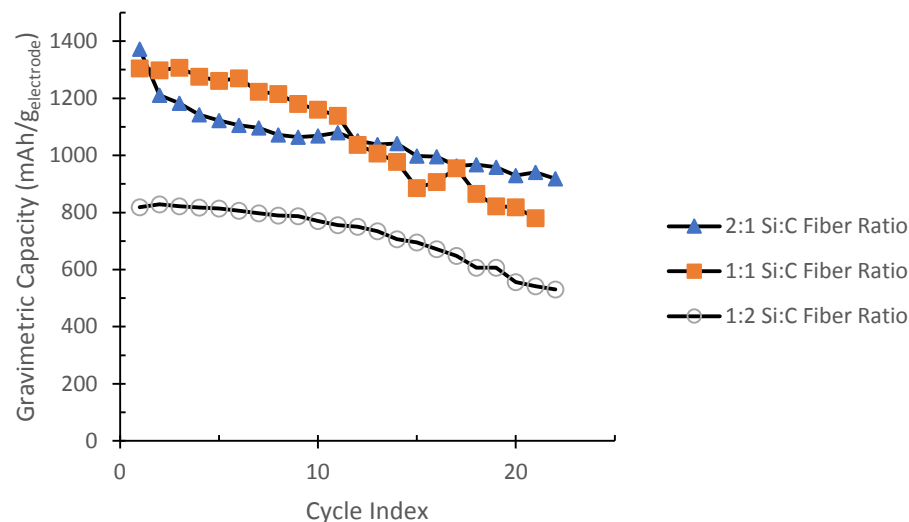
2:1 Si/PAA:C/PAA fiber ratio



After compaction – the fiber mat vol. fraction was 0.25-0.40 (not as high as a single Si/C/PAA fiber mat)

Electrochemical Performance of Si/PAA-C/PAA Dual Fiber Anodes

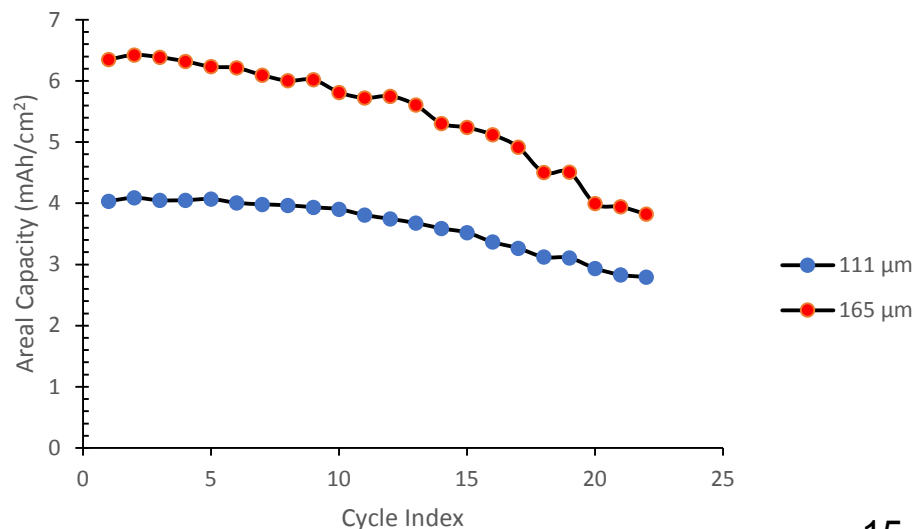
- Anodes were characterized in CR2032 half-cells with a Li metal cathode and an electrolyte of 1.2 M LiPF₆ with 3/7 EC/DEC and 30% FEC.
- Initial reversible capacities were high (3,100-3,360 mAh/g of Si)
- For a 1:2 Si:C dual fiber mat, two thicknesses were examined: 111 μm and 163 μm . The areal capacities for these two anodes was very high, at 4.0 and 6.5 mAh/cm².
- Capacity fade of the dual fiber mats was attributed to insufficient compaction/welding of the dual fiber mat.
- Si/PAA single fiber mat (no C/PAA fibers) exhibited no capacity



Significance of Results: Good Si utilization was achieved without adding an electrical conductor to the Si fibers. C/PAA fibers provided electron transport pathways throughout the fiber mat anode.

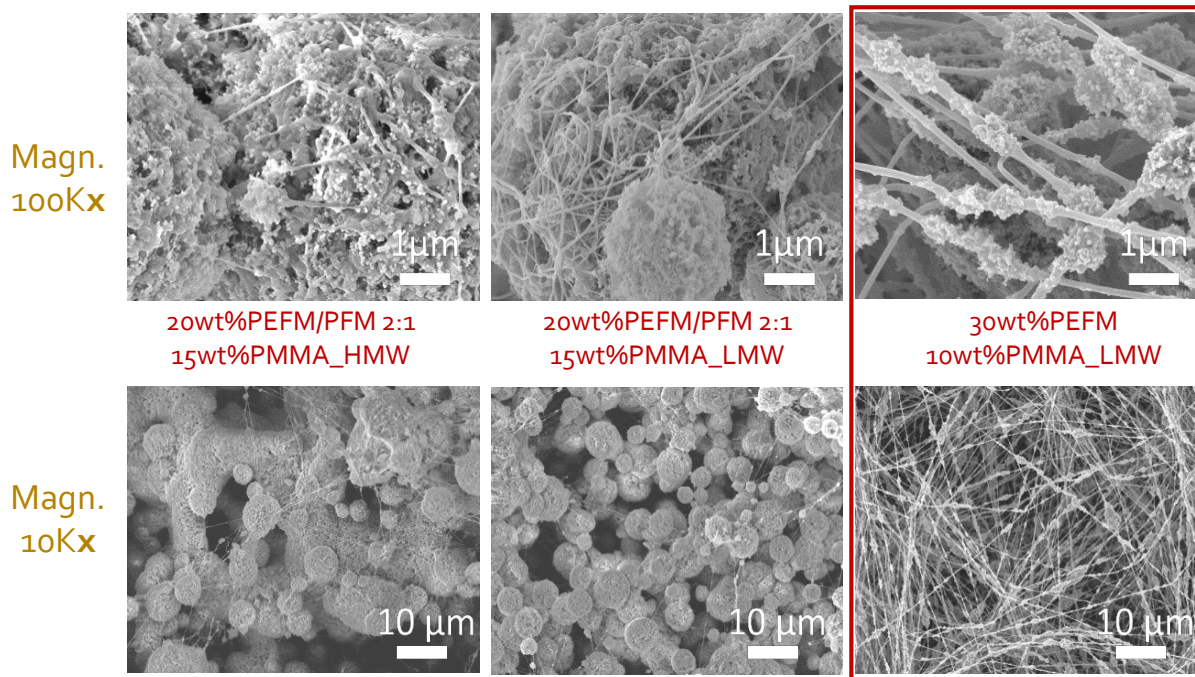
Next Experiments: Stop/minimize capacity fade during cycling.

1. Improve the quality of the carbon fibers
2. Optimize the fiber composition and ratio
3. Improve mat compaction and welding
4. Replace Si/PAA fibers with Si/PEFM fibers.



Electrospinning of Si/PEFM with PMMA as a Carrier Polymer

- Electrospun fibers could not be made with an ink of Si+PEFM.
- Electrospinning of Si/PEFM fibers was observed when low MW PMMA carrier (10 wt%), was added to an ink containing 60 wt% Si and 30 wt% PEFM.



The Si nanoparticle distribution in the electrospun fibers is not perfect and so we are continuing to investigate the Si/PEFM/PMMA system.

Response to Previous Year Reviewers' Comments

This approach appears to have volumetric energy density issues (Reviewer 3)

Volumetric and areal energy densities were carefully calculated for all battery tests with nanofiber electrodes. For single fiber electrodes, we achieved volumetric energy densities in the 475-750 mAh/cm³ range. The areal capacities were 1.0-4.5 mAh/cm² (see slides 8 and 9).

Electrospun Si nanoparticles in a fiber shape has been investigated by other researchers for many years...the thickness of the electrode is still a challenge. (Reviewer 5)

As correctly noted by the reviewer, our nanofiber electrodes have a polymer binder and we compact and weld the fiber mats to increase the fiber volume fraction and strengthen the mat. Our electrodes have a much high fiber volume fraction than pyrolyzed carbon fiber mats. We make thick electrodes and effectively utilize the entire fiber mat, as shown by the high areal capacity data for our dual fiber anode in slide 15, where areal capacity data are shown for 111 μm and 163 μm thick anodes.

The reviewer identified that one problem has to do with the evaluation of Si nanoanodes in half-cells ... The performance of Si nanoanodes in a full cell is more challenging (Reviewer 2)
Full cell results with a Si/C/PAA nanofiber mat anode and a LiCoO₂/C/PVDF nanofiber mat cathode are shown on slide 9.

The reviewer liked the novelty of the approach, but was concerned about cost (Reviewer 4)

The PI has visited eSpin Technologies, Inc. (Chattanooga, TN) and discussed manufacturing costs with its president, Dr. J. Doshi. The electrospinning process is fast and compatible with roll-to-roll Li battery electrode manufacturing schemes. Electrospinning equipment is available for commercial manufacturing. eSpin has used electrospinning to manufacture a range of commercial products, including air filters for homes and hospitals. We estimate that electrospinning will add a few dollars per m² to the anode cost. A more detailed cost analyses will be performed in Year 3.

Collaborations

- **Lawrence Berkeley National Laboratory (Dr. Gao Liu):** Synthesize conductive polymer binders which are sent to Vanderbilt University for electrospinning.
- **Oak Ridge National Laboratory (Dr. Jagjit Nanda):** Conduct electrochemical performance analysis of nanofiber anodes and provide microstructural and interfacial characterization of the electrospun materials.
- **e-Spin Technologies, Inc. (Dr. Jayesh Doshi):** Conduct preliminary scale-up of the electrospinning process at his commercial facility in year 3.

Remaining Challenges and Barriers

1. Creating Si/PEFM mats with well-formed fibers, 55-60 wt% Si nanoparticles with an average diameter $< 1\ \mu\text{m}$.

- Requires further optimization of ink composition and electrospinning conditions
- How important is fiber diameter?
- Will such mats work as well as a slurry anode with the same Si/PEFM composition?

2. Optimizing the fiber composition and mat morphology of a dual fiber anode to achieve high gravimetric, volumetric, and areal capacities?

- Will PEFM binder for Si fibers work better than PAA?
- Is there an optimized interfiber void space in a dual fiber mat that will accommodate Si volume changes so that there will be no physical disintegration of the fiber structure during charge/discharge cycling?
- How does capacity retention with charge/discharge cycling and capacity vs. C-rate correlate with dual fiber mat thickness and porosity?
- Can an electrospun dual fiber mat with an optimized porosity, a well-adhering Si binder and separate fibers for electrical conduction overcome the mechanical fracture, unstabilized SEI, and poor electrode integrity challenges of Si based anodes in Li-ion batteries.?

3. Achieving high fiber mat anode performance in a coin cell

- Demonstrate a Si-based anode discharge capacity above 750 mAh/g, after 50 cycles at 0.1C and a capacity above 500 mAh/g after 50 cycles at 1C.

Future Work

- Improve carbon fiber quality (distribution of carbon nanoparticles within a PAA fiber) during dual fiber electrospinning. Examine different carbon powders and different polymer binders for the carbon fibers.
- Study the effects of dual fiber morphology on Si anode capacity and capacity retention.
 - Look at different ratios of Si and C fibers
 - Look at different Si particle contents in the Si/PAA fibers
 - Improve mat compaction and welding procedures to obtain dual fiber mats with a fiber volume fraction of at least 0.40.
 - Examine anodes of different thickness, to give areal capacities of 1.0, 2.0, and 4.0 mAh/cm²
 - Determine anode capacity as a function of C-rate (from 0.1C – 2C)
- Continue to work on electrospinning Si/PEFM fibers. Identify the electrospinning conditions that give well-formed fibers with 55-60 wt% Si particles.
- Prepare and test an anode with electrospun C/PAA fibers and electrospayed droplets of Si/PEFM or Si/PFM (60-70 wt% Si in the droplets).

Any proposed future work is subject to change based on funding levels.

Summary and Conclusions

A new electrically conducting polymer binder has been synthesized.

- PEFM is a modified version of PFM
- As an anode binder with Si nanoparticles, good charge/discharge performance was achieved with a high concentration of PEFM binder (the maximum PEFM for a working anode is 45 wt% vs. 33 wt% for PFM).

A new dual fiber anode mat morphology was created and successfully tested.

- Separate fibers were electrospun, for Li intercalation (Si/PAA fibers) and for electrical conduction (C/PAA fibers)
- Good charge/discharge behavior was observed (essentially complete utilization of Si) for thin and thick fiber mats (up to a thickness of 165 μm).
- Results show that there are sufficient contact points between Si/PAA fibers and C/PAA fibers in a dual fiber mat for good isotropic electron flow throughout the anode, with good electrolyte infusion between fibers. 33% carbon fibers in a dual fiber mat is sufficient for good electron conduction.
- The carbon fiber morphology in a dual fiber mat was poor (additional work is needed to improve the fiber quality); the Si/PAA fiber morphology was good.

Single fiber Si/C/PAA anode mats performed well in baseline half-cell and full-cell tests.

- A Si/C/PAA weight ratio fiber composition of 25/40/35 worked well, with an initial effective gravimetric capacity of 950 mAh/g (based on the total anode weight), a volumetric capacity of 476 mAh/cm³, and an areal capacity of 1.89 mAh/cm² at 0.1C. Capacity fade upon charge/discharge cycling was small.

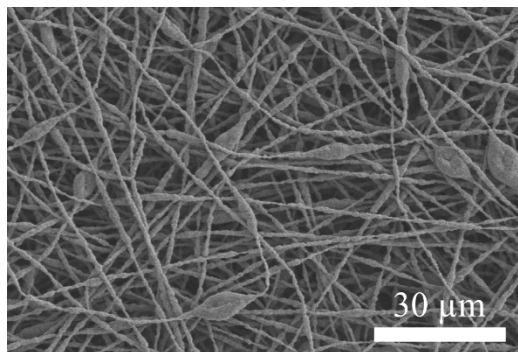
To date, all project milestones have been met on schedule.

Technical Back-Up Slides

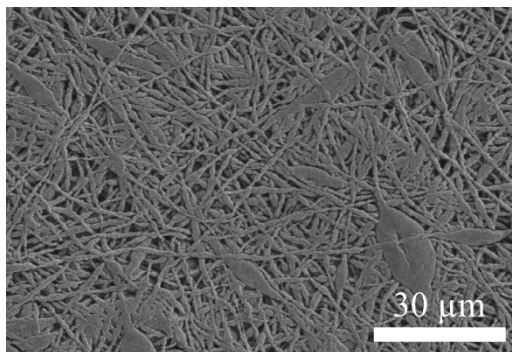
Fiber Mats With/Without Compaction and Welding

After electrospinning, Si/C/PAA fiber mats were compacted (at 90 MPa for 40 seconds) and welded (exposure to MeOH vapor for 1 hour) to improve interfiber connectivity. A similar procedure was used for dual fiber mats.

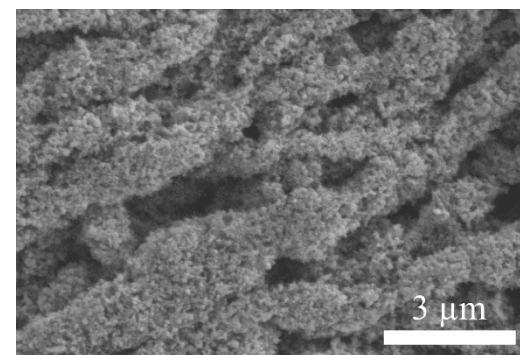
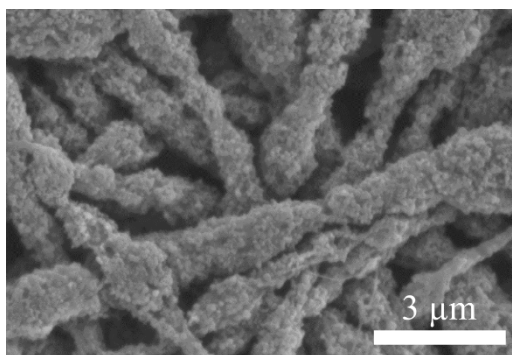
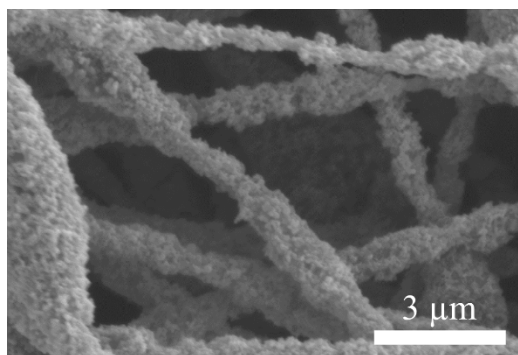
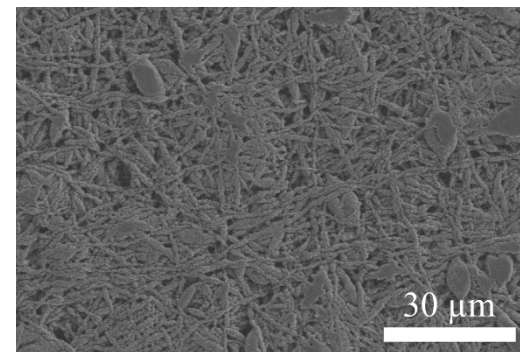
As-Spun Fibers
(~25% fibers)



Compacted Fibers
(~80% fibers)



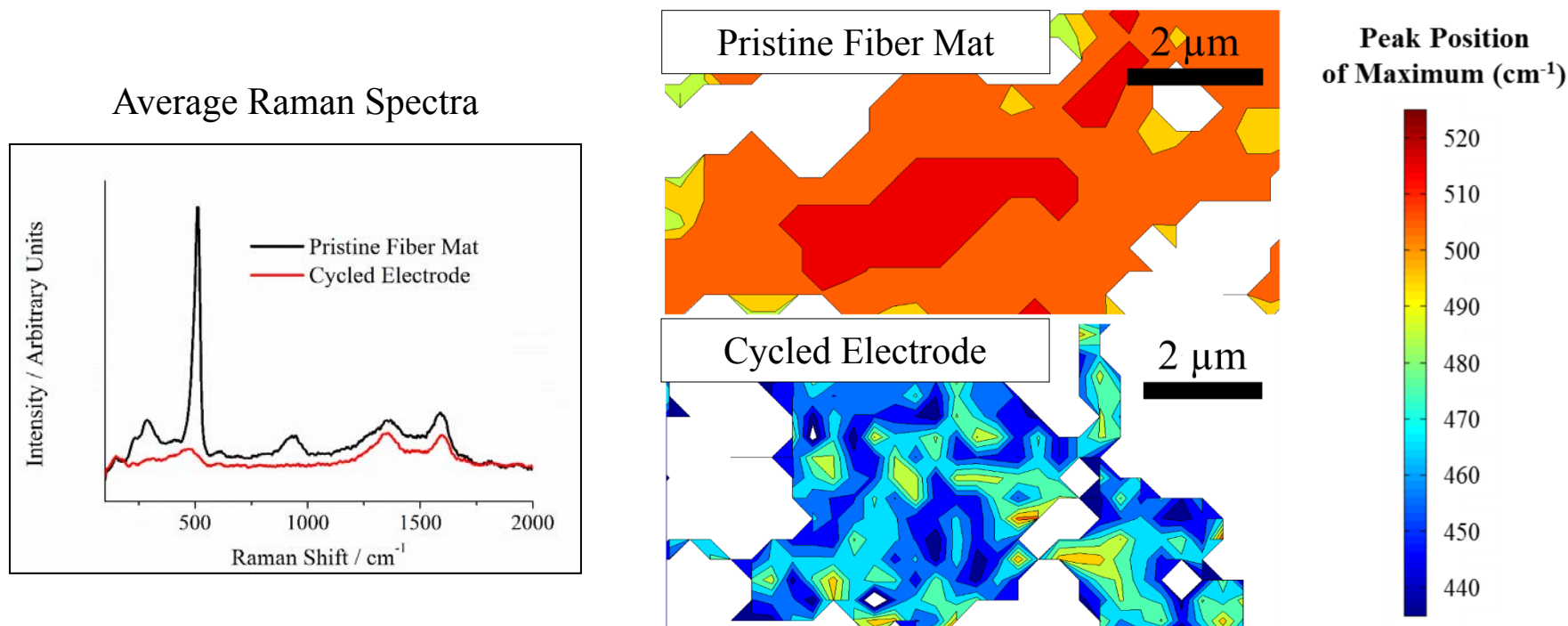
Compacted/Welded Fibers
(~80% fibers)



Fiber volume fractions of compacted and compacted/welded anodes are similar, but electrical resistance was reduced after welding, indicating better fiber contact.

Raman Spectroscopy of Si/C/PAA Fiber Mats

The Raman spectra of pristine fiber mats were compared to that of post-mortem electrodes (cycled 50 times at 0.1C) to evaluate structural changes which occurred during electrochemical cycling.



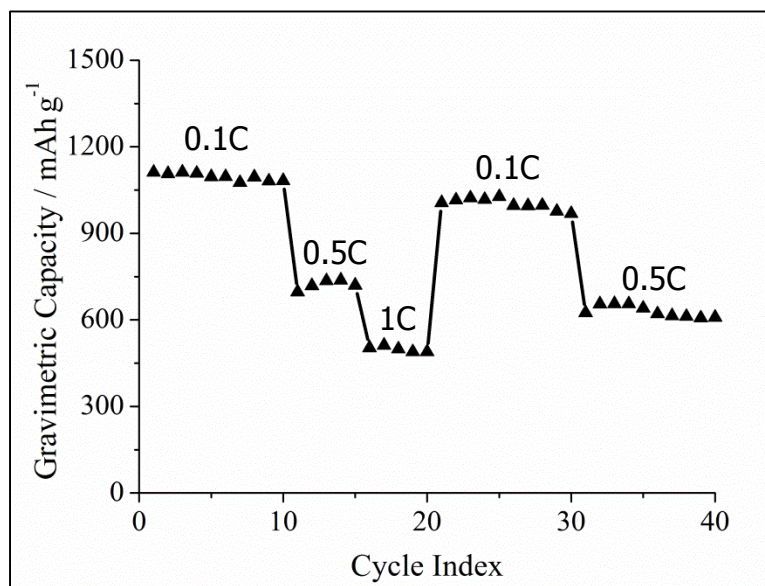
*Experiments conducted by Rose Ruther at ORNL.

Results: Pristine fiber mats contained crystalline Si which was converted to amorphous Si during cycling. This observation is consistent with the shape of the charge/discharge curves of the Si/C/PAA fiber mats.

Rate Capabilities of Electrospun Si/C/PAA Anodes

An electrospun Si/C/PAA fiber mat anode was tested at charge/discharge rates up to 1C

- Composition: Si/C/PAA in a 40/25/35 weight ratio
- Anode had a fiber volume fraction ~ 0.85 and welded interfiber contacts
- Cell was cycled for 5 – 10 cycles at 0.1C, 0.5C, and 1C
- This rate capability study was conducted after cycling the fiber mat for 40 cycles at 0.1C



Results: The fiber mat anode had good rate capabilities with 489 mAh/g at 1C (i.e., 45% capacity retention at 1C). These results demonstrate that excellent progress is being made toward one milestone (750 mAh/g at 0.1C and 500 mAh/g at 1C).